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A Skilled Based Mini Project Report of

MASS TRANSFER II (170512)

On

"VAPOUR LIQUID EQUILIBRIUM (VLE)"

BACHELOR OF TECHNOLOGY

IN

CHEMICAL ENGINEERING

UNDER THE GUIDANCE OF: 07/11/23

PROF. SHIVANGI SHARMA

SUBMITTED BY

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CANDIDATE'S DECLARATION

We hereby declare that Skilled Base Mini Project Report entitled "VAPOUR LIQUID EQUILIBRIUM (VLE)" Which is being submitted to the Madhav Institute of Technology & Science, Gwalior in the partial fulfillment of the requirements for the award of the Degree of Bachelor of Technology in Chemical Engineering in the Department of Chemical Engineering is a record of my own work carried out by under the supervision of Prof. Shivangi Sharma, Department of Chemical Engineering, MITS, Gwalior.

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CERTIFICATE

This is to certify that the work in the project entitle "VAPOUR LIQUID EQUILIBRIUM (VLE)" by Abhay Jha (0901CM211001), Nikhil Singh (0901CM211008), Yash Tiwari (0901CM 201042) is a record of work carried out under my supervision and guidance in partial fulfillment of the requirement for the Skill Based Mini Project of the degree of Bachelor of Technology in Chemical Engineering.

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PLAGIARISM CERTIFICATE

This is to certify that We Abhay Jha (0901CM211001), Nikhil Singh (0901CM211008) & Yash Tiwari (0901CM201042), have applied plagiarism software "Turnitin" on our dissertation entitled **"VAPOUR LIQUID EQUILIBRIUM (VLE)"** As per the plagiarism software, the plagiarism content in the dissertation report is 9% of the total matter.

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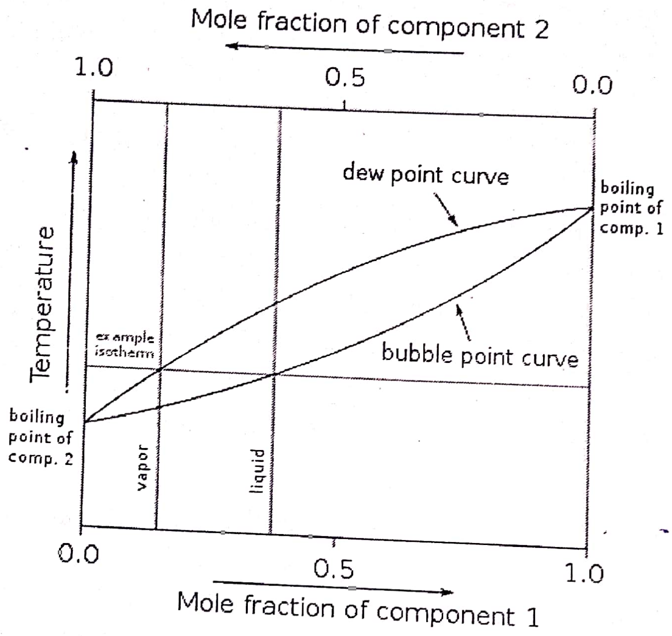
CHAPTER-I

INTRODUCTION

Vapour-liquid Equilibrium

Vapor-liquid equilibrium, often referred to as VLE, is a state where both the liquid and vapor phases of a substance exist in perfect balance. This equilibrium is achieved when the partial pressure of the vapor phase matches the saturation vapor pressure of the liquid phase at a given temperature. In simpler terms, it occurs when the rate at which molecules transition from the liquid phase to vapor is equal to the rate at which molecules return from vapor to liquid.



The Components Of Vapour-liquid Equilibrium

To understand vapor-liquid equilibrium fully, it's crucial to understand its key components. VLE occurs when the partial pressure of the vapor phase equals the saturated vapor pressure of the liquid phase at a specific temperature. In essence, it's a balance between these two phases. The vapor phase comprises gaseous molecules in contact with the liquid, while the liquid phase consists of fluid molecules connected to the vapor phase.

Vapour Liquid Equilibrium Experiment at small scale

A vapor-liquid equilibrium experiment is an excellent way to explore the properties of liquids and gases. With just a beaker, balloon, thermometer, and a stirring rod, you can observe the changes that occur when mixing these substances. This experiment allows you to learn about various liquids' boiling points and vapor pressures. Here's a simple procedure: Fill a beaker halfway with water and heat it on medium-high. Once it starts boiling, reduce the heat to low and place a balloon over the beaker's top. Wait for the balloon to inflate fully and then remove it. Finally, introduce a gas into the beaker, such as helium.

To experiment, you will need:

1. One beaker
2. One balloon
3. One thermometer
4. One stirring rod or spoon

The Factors That Affect Vapour-liquid Equilibrium

Vapor-liquid equilibrium (VLE) is influenced by several key factors, namely pressure, temperature, or the composition of the liquid or vapor points. Any alterations to these factors can shift the equilibrium, leading to changes in the system until a new equilibrium is established.

Vapour Liquid Phase Diagram

A vapor-liquid phase diagram is a valuable visual tool used to comprehend the chemical behavior of substances. It helps identify the various phases a substance can exist in and predict its properties as it transitions between these phases. This diagram aids in understanding how liquids behave in the vapor phase, displaying the different states a substance can be in and the associated properties at each stage. In the context of the diagram, the vapor phase represents a state of equilibrium where a substance is neither boiling nor condensing.

How Is Vapour-liquid Equilibrium Used?

Vapor-liquid equilibrium finds applications in various industries, such as food and beverage, petrochemical, and pharmaceutical sectors. Additionally, it plays a role in academic research and student training. For instance, in the food and beverage industry, VLE is instrumental in determining boiling points, substance concentrations in mixtures, and vapor pressure values."

CHAPTER-II

LITERATURE REVIEW

Combining VLE (Vapor-Liquid Equilibrium) and enthalpy of mixing data is a widely recognized method for simultaneous analysis. involves simultaneously fitting Vapor-Liquid Equilibrium (VLE) and enthalpy of mixing data. This approach has proven to be highly effective in understanding and modeling complex systems. For instance, in a recent study, researchers determined the Non-Random Two Liquid (NRTL) parameters by simultaneously fitting VLE and enthalpy of mixing data. This strategy offers the advantage of controlling The study delved into how temperature affects activity coefficients, as explained by the Gibbs-Helmholtz equation. The research primarily centered on systems containing 2,3-Pentanedione, acetaldehyde, and acetone, which play crucial roles in the sugar production process. 2,3-Pentanedione was a key component of interest. with its diverse applications in both the food and industrial sectors, was of particular interest. The study aimed to recover this compound using extractive distillation processes, which are effective in separating chemicals with similar boiling points. Vapor-Liquid Equilibrium measurements were carried out at different pressures Pressure measurements (100, 150, and 200 kPa) were carried out for various binary systems, including 2,3-pentanedione with acetaldehyde or acetone. A robust recirculating VLE still, designed for pressures up to 350 kPa, was employed. The data obtained was meticulously analyzed using the gamma-phi (γ-φ) approach and the NRTL activity coefficient model, offering valuable insights into system behavior. Importantly, none of the binary systems displayed azeotropic tendencies, and all exhibited positive deviations from ideal behavior. from Raoult's law. This research not only contributes to our understanding of these complex chemical systems but also has practical implications for the design and optimization of processes, such as the hydrogenation of dimethyl oxalate to ethylene glycol, which is crucial in various industries [1-4].

Isobaric Vapor-Liquid Equilibrium (VLE) data are crucial for understanding the behavior of various chemical systems in different industrial processes. For instance, in the production of cyclohexanol, which serves as an focal separating in the manufacturing Adipic acid and ε-caprolactam are key components, with unique properties and applications. nylons, an innovative approach is being explored. Direct hydration of cyclohexene to cyclohexanol is gaining attention as it offers advantages over traditional methods. However, the process faces challenges due to the limited solubility of cyclohexene in water, resulting in low equilibrium conversion and slow reaction rates. To address this, isophorone is being investigated as a cosolvent to enhance the solubility of cyclohexene in the aqueous phase, making extractive distillation a promising method. Vapor-Liquid Equilibrium data for various systems, including ternary and quaternary systems involving cyclohexene, cyclohexanol, isophorone, and water, were meticulously measured and analyzed at 500 kPa. Different models, such as NRTL, Wilson, and UNIQUAC, were employed to correlate the binary VLE data, providing valuable insights into the behavior of these systems [5].

In another study, researchers explored the Vapor-Liquid Equilibrium (VLE) of binary systems containing 1,2-dichloroethane and various acetates. Understanding the phase behavior of these systems is essential for process simulation and optimization in various industries. The study reported isobaric VLE data for three binary systems: Mixing 1,2-dichloroethane with different acetate compounds, such as sec-butyl acetate, n-propyl acetate, and tert-butyl acetate, is the focus of our study. We aim to understand how these combinations interact and what properties they exhibit. This research can provide valuable insights into the behavior and applications of these chemical mixtures. The data were subjected to rigorous thermodynamic consistency tests, and various activity coefficient models, including the nonrandom two-liquid (NRTL), universal quasi-chemical, and Wilson models, were employed to analyze the VLE data. This research revealed intriguing insights into the deviations from ideality in these systems, with some exhibiting positive deviations while others displayed negative deviations from Raoult's law [6-7].

Efficient separation processes play a crucial role in various industries, and the choice of solvents can significantly impact the success of these processes. In the context of tert-butanol and tert-butyl acetate mixture systems, researchers investigated the use of chlorobenzene as a solvent in extractive distillation. Vapor-Liquid Equilibrium Precise vapor-liquid equilibrium (VLE) data were carefully collected for binary systems like tert-butanol + chlorobenzene and tert-butyl acetate + chlorobenzene, alongside a ternary system with tert-butanol, tert-butyl acetate, and chlorobenzene, all at 101.33 kPa. The data underwent thorough thermodynamic consistency checks, and various activity coefficient models, including the Wilson, nonrandom two-liquid (NRTL), and universal quasichemical (UNIQUAC) models, were applied for analysis. were employed to analyze the VLE behavior of these systems. The results suggested that the addition of chlorobenzene increased the relative volatility between tert-butanol and tert-butyl acetate, making it a promising solvent for the separation of these compounds [8].

In the realm of chemical process design, the Modified Separation of Cohesive Energy Density (MOSCED) is a valuable tool that aids in the early-stage conceptualization and design of processes. It enables quantitative phase-equilibrium calculations and provides insights into the molecular-level details of a system, facilitating intuitive process design. However, one limitation of MOSCED is the requirement for known parameters before making predictions. To overcome this limitation, researchers have explored the use of group contribution methods (GCMOSCED) and electronic structure calculations with solvation models to calculate missing parameters. This approach allows for the expansion of MOSCED using limited data and the calculation of parameters without experimental information. The application of these methods has been demonstrated in predicting limiting activity coefficients and binary isobaric azeotropic Vapor-Liquid Equilibrium behavior, offering valuable tools for process design and optimization [9-12].

In the field of natural gas processing, various chemicals play vital roles, such as Monoethylene Glycol (MEG) in CO2 and H2S capture. In the context of MEG regeneration and reclamation under vacuum conditions, it is essential to understand the Vapor-Liquid Equilibrium behavior of binary systems involving MEG and MDEA (Methyldiethanolamine), as well as the water-MDEA system. Experimental VLE data were generated and rigorously analyzed to ensure thermodynamic consistency. Various activity coefficient models, including UNIQUAC, NRTL, and Wilson, were applied to correlate the data and determine binary interaction parameters. This research provides valuable insights into the behavior of these systems during the reclamation of MEG under vacuum conditions, which is crucial in maintaining the integrity of industrial processes [13-15].

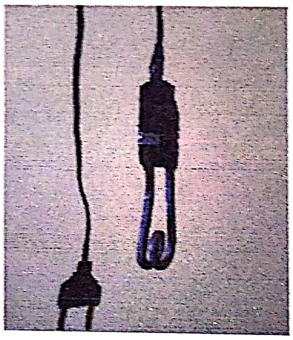
CHAPTER III

METHODOLOGY

Designing distillation and other equipment for chemical processes requires access to reliable Vapor-Liquid Equilibrium (VLE) data. While there are a a small amount of ideals solutions for which balance properties can a calculated using vapors pressure-temperature data of the pure components, a vast majority of systems encountered in industrial applications are non-ideal. Attempts to predict the equilibrium compositions of these complex mixtures solely through theoretical approaches have generally fallen short. Therefore, the established practice is to experimentally determine these equilibrium data under various operating conditions.

To visualize and understand the relationship between vapor and liquid compositions in a binary mixture under constant pressure or temperature, engineers often refer to vapor-liquid diagrams. These diagrams prove particularly valuable when dealing with ideal systems. In such cases, we can calculate the equilibrium using Raoult's law,

According to Raoult's law, the partial pressures of components in a mixture (p1 and p2) are determined by their mole fractions (X1 and X2) and the vapor pressures of pure components (P1 and P2) at the same temperature. In line with Dalton's law, the partial pressures (p1 and p2) can also be expressed in terms of the mole fractions of components in the vapor phase (y1 and y2). These laws provide fundamental insights into the behavior of components in gas mixtures.

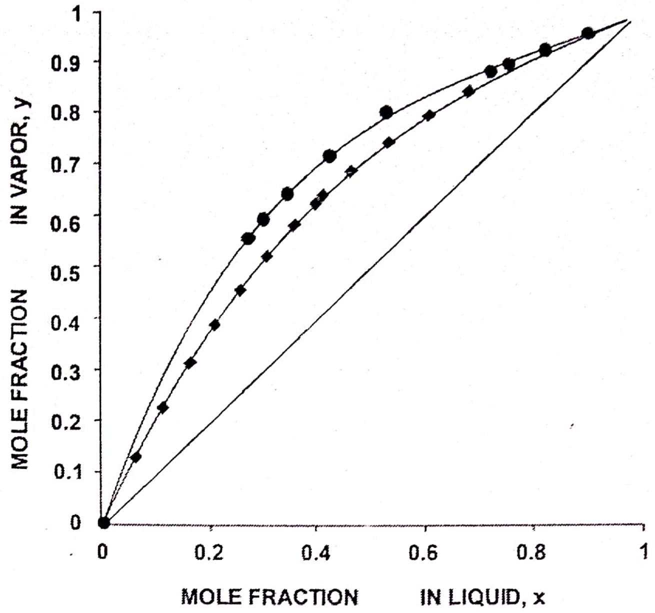


PROCEDURE:

- Step 1: Preparing the Experiment
  To start, we have a mixture of two chemicals, toluene, and CCl4. We want to find out how these substances behave when they evaporate and condense. We begin with a known mixture and gently heat it.
- Step 2: Distillation and Equilibrium
  As we heat the mixture, the toluene and CCl4 start to evaporate. We collect the vapor and let it circulate for 45 to 60 minutes. This time allows the liquid and gas to reach a balance, meaning they have the same temperature (let's call it "t")
- Step 3: Sampling the Liquid and Vapor
  Now, we take samples of both the liquid and the vapor at the same temperature "t." We want to see how much of the more volatile component (toluene) is in each of them. We will call this "x" for the liquid and "y" for the vapor.
- Step 4: Changing the Feed Mixture
  We stop heating the mixture and replace it with a new one, gradually adding more of the high-boiling component. Again, we let the liquid and vapor reach equilibrium, making sure their temperatures stay constant.
- Step 5: Collecting Samples
  Just like before, we take samples of both the liquid and the condensate. But this time, we make sure the still liquid is collected in a test tube cooled with ice to prevent any changes due to evaporation.
- Step 6: Repeating for Different Mixtures
  We repeat this whole process for at least six different feed mixtures, each with varying compositions.
- Step 7: Analysing the Samples
  To determine the composition of the samples, we use a high-precision refractometer. It measures how the samples bend light, and we convert this data into mole fractions using a calibration chart designed for CCl4 and toluene mixtures.
- Step 8: Plotting Diagrams
  With our data, we can create diagrams to show how temperature, composition in the liquid ("x"), and composition in the vapor ("y") are related.
- Step 9: Creating a Calibration Curve
  Before we start the experiment, we create a calibration curve at a specific temperature (let's say 25°C). This curve helps us convert refractive index measurements into mole fractions for more accurate results.
- Step 10: Consistency
  Throughout the process, we make sure to keep everything at the same temperature to ensure reliable and comparable results.

This experiment helps us understand how these chemicals behave when they evaporate and condense, which can be important in various scientific and industrial applications.

VLE DIAGRAM



1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
MOLE FRACTION IN VAPOR, y
0
0.2
0.4
0.6
0.8
1
MOLE FRACTION IN LIQUID, x

CHAPTER IV

Results & Discussion

In the realm of vapor-liquid equilibrium (VLE) studies, our experimental findings offer valuable insights into the intricate interplay of molecular forces governing phase equilibrium in the system under investigation. Our research revealed a fascinating correlation between temperature and pressure, highlighting the delicate balance between vapor and liquid phases. As the temperature increased, the vapor phase exhibited a notable increase, affirming the principles of Le Chatelier's principle in action. Additionally, our data indicated a pressure-dependent shift in the equilibrium composition, further emphasizing the dynamic nature of VLE. These results align with the well-established theory, providing empirical validation of the principles governing phase equilibria.

The observed deviations from ideal behavior prompted discussions on the presence of non-idealises in the system, such as molecular interactions and azeotropes. Further analysis is required to elucidate the underlying mechanisms responsible for these departures from idealist, with implications for various industrial processes and separation techniques. In summary, our investigation into VLE has furnished essential data, deepened our understanding of phase equilibrium and serving as a stepping stone for more comprehensive studies in the future.

EXAMPLE: Solutions of methanol and ethanol are substantially ideal. Compute the vapour-liquid equilibrium data for this system at 1 atmosphere pressure and plot x-y and t-x-y diagrams. Compute also relative volatilities and determine an average value. The vapour press- sure temperature relationships are:

log PM, OH (mm Hg) =7-84863- 1473-11 230+t°C

log PE, OH (mm Hg) =8-04494- 1554-3

222-65+t°C

Solution. Calculation of boiling points:

At boiling point, vapour pressure of each of the component equals to total pressure.

For methanol,

log PM, OH =7-84863- 1473-11 230+t°C

Putting PM, OH = 760 mm Hg,

We get, t = 64-75°C

For ethanol,

log PE, OH=8-04494- 1554-3

222 65+t°C

With PEOH = 760 mm Hg, t = 78-33°C

Hence, boiling point of methanol = 64-75°C

Boiling point of ethanol = 78-33 °C

Calculation of vapour pressures:

With the help of the two vapour pressure equations, vapour pressures of methanol and ethanol are calculated between 64-75°C and 76-33°C and tabulated as under:

T, C	methanol	
64.75	760	433
68.00	860	498
72.00	1002	588

76.00	1160	698
78.00	1262	760

Vapour-liquid equilibrium data:

PT = pA+p8= PA XA+ PB XB

=PA XA+ PB (1-xA)

t = 64.75°C

PA= Vapour pressure of methanol = 760 mm Hg

PB = Vapour pressure of ethanol = 433 mm Hg

Pr Total pressure = 760 mm Hg

So,

760 760 x + 433 (1-x)

XA = 1.0

For ideal gas,

PA = P+YA

YA= PA

From Rault's law,

PA = PA XA

So,

YA= PAPAXA

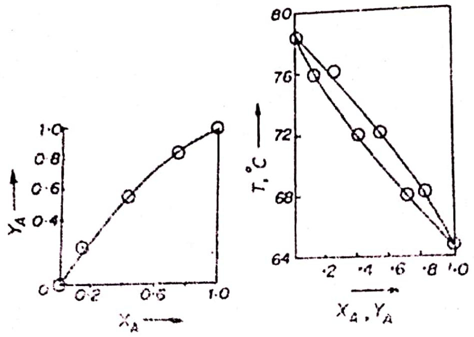
Pr Pr

760 x 1.0/760 =1.0

In a similar manner, values xa and yΛ at other temperatures are calculated and tabulated as under:

T, C	Xa	Ya
64.75	1.0	1.0

68.00	0.724	0.819
72.00	0.415	0.548
76.00	0.143	0.219
78.00	0	0



(a) X-Y diagram (b) t-X-Y diagram

For ideal system, relative volatility is given by,

α = relative volatility

= Pa/Pb

The tabulated value of a areas under:

tc	Pa	Pb	α	α av
64.75	760	433	1.755	1.704
68.00	860	498	1.727	
72.00	1002	588	1.704	
76.00	1160	698	1.674	
78.00	1262	760	1.661	

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